THE SYNTHESIS OF CERTAIN FATTY ACIDS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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INTRODUCTION

The work herein described was taken up in an attempt to prepare capric acid from lauric acid. It was a part of a general problem undertaken in the Division of Analytical Chemistry at the request of the National Research Council. The problem included the preparation of pure fatty acids which occur naturally in fats, and the synthesis of their cholesterol esters for use in certain studies in immunization, being carried out under the direction of the research council. The acids to be prepared were butyric, caproic, caprylic, capric, lauric, myristic, palmitic, oleic, linolic and clupanadonic acids. All of these acids were successfully prepared. Butyric acid was made by the oxidation of normal butyl alcohol. Caproic acid was obtained by a malonic ester synthesis with normal butyl bromide. Caprylic and lauric acids were obtained from cocoanut oil, myristic acid from nutmeg butter, oleic acid from olive oil, linolic acid from cottonseed oil and clupadonic acid from menhaden oil. Repeated efforts to find a natural source of capric acid were of no avail. Its preparation was taken up in two ways: (1) By building up from caprylic acid, and (2) By degradation from lauric acid. The writer was assigned the problem of breaking down lauric acid to form capric acid.

The fatty acids are those aliphatic monocarboxylic acids which are found in nature as esters of glycerol, or glycerides, in which form they are called fats. By saponification, i.e., treating a fat with strong alkali, one obtains glycerol, and a mixture of soaps, the metallic salts of the acids whose glycerides compose the fat. The acids may be separated by esterifying the fatty acid mixture obtained by saponification and fractionating the resultant mixture of esters. The acids of the acetic series, of the general formula $C_nH_{2n+1}COOH$ are widely distributed in nature.

Acetic acid,[1] CH_3COOH, the first of the series to occur in fats is found as a mixed glyceride in the seeds of the spindle tree. It has also been found in butter fat and Macassar oil, but is usually prepared, either from the pyroligneous acid obtained in the distillation of wood, or as vinegar by the acetous fermentation of alcoholic liquids. Glacial, or pure acetic acid gives on cooling, a colorless, crystalline mass, melting at 17.6°C. and boiling at 119.0°C.

Butyric,[1] $CH_3(CH_2)_2COOH$ occurs in butter fat in which it is found in the form of a mixed glyceride to the extent of about six percent. It is a colorless liquid and when freshly distilled, smells like acetic acid. Its aqueous solution recalls the odor of rancid butter. It crystallizes at -19°C; the crystals melt at -65°C. The acid boils under ordinary pressure at 162.3°C. It is miscible with water, alcohol, and ether in all proportions. Chromic acid oxidizes butyric acid to

acetic acid and carbon dioxide. Alkaline permanganate oxidizes it completely to carbon dioxide and water.

Caproic acid,[1] $CH_3(CH_2)_4COOH$, was discovered in 1818 by Chevreul. He obtained its glyceride from butter, cocoa nut, and palm nut oils. It is slightly soluble in water, but not miscible with it. It melts at -8°C, and boils at 202-203°C at 770 mm. pressure. Its odor is like that of prespiration.

Caprylic acid,[1] $CH_3(CH_2)_6COOH$ occurs in butter fat, and notably in cocoa nut and palm nut oils. It is a liquid at ordinary temperatures, and crystallizes at 12°C in laminae, melting at 16.5°C. It is only slightly soluble in water.

Capric acid,[1] $CH_3(CH_2)_6COOH$, occurs in the milk fats of the cow, and the goat, in the fat from Lindera Benzoin, palm nut oil, fusel oil[2] and oil of rue[3]. According to Görgey,[4] Lewkowitsch,[5] and others, cocoanut oil contains over 10% of capric acid. Repeated fractionations of methyl and ethyl esters from large amounts of cocoanut oils of different grades, and from different sources, have been carried out at the University of Illinois. In none of these has more than a trace of ester been obtained corresponding to the esters of capric acid. Apparently the mixture of caprylic and lauric esters which comes over at first, has been mistaken for the capric ester. If this mixture be carefully distilled under diminshed pressure, it becomes resolved into its two component esters. The acid crystallizes in fine white needles melting at 31.3°-31.4°C, and boiling at

268-270°C under ordinary pressure, 153-154°C under 13 mm. pressure. The acid is almost insoluble in water, and has a goat-like odor, which becomes more distinct at the temperature of its melting point. The alkali caprates are easily soluble in water. Barium caprate crystallizes from boiling water, in which it is very sparingly soluble, in laminae. The salt is easily soluble in boiling alcohol.

Lauric acid,[1] $CH_3(CH_2)_{10}COOH$ is found in considerable quantities in tangkallak fat[6], dika fat[6], and laurel oil.[7,8] Cocoa nut oil[9,10,11] and palm nut oil also contain notable proportions of laurin. Kusu oil[12] consists for the most part of the triglyceride of lauric acid. The acid is best prepared from laurin[13] obtained by recrystallizing tangkallak fat from ether, and saponifying that glyceride, or from cocoanut oil by preparing its methyl esters and fractionating the mixed methyl esters.[14] At the ordinary temperature the acid is solid and crystallizes from alcohol in needles melting at 43.6°C. It is the first acid of the acetic series that cannot be distilled at ordinary pressure without undergoing (slight) decomposition. It boils at 225°C under 100 mm. pressure, 176°C under 15 mm., 102°C in vacuo. Lauric acid is slightly soluble in large quantities of boiling water. It has been repeatedly pointed out that lauric acid occupies an intermediate position between the soluble and the insoluble fatty acids.

Myristic acid,[1] $CH_3(CH_2)_{12}COOH$ occurs as the glyceride in

nutmeg butter. Lewkowitsch[15] has shown that "Ochoco fat"[16,17,18] consists of practically pure myristin. The acid crystallizes in laminae melting at 53.8°C, boiling at 250.5°C under 100 mm., and at 121-122°C in vacuo. The acid is insoluble in water but may be distilled under pressure with superheated steam. It is difficultly soluble in alcohol and ether.

Palmitic acid,[1] $CH_3(CH_2)_{14}COOH$, occurs in most vegetable and animal fats. It was first isolated in the pure state from palm oil.[19] It is also found in Chinese vegetable tallow,[20] in spermaceti[21] ascetyl palmitate, in beeswax,[22,23] as myricyl palmitate, and in opium wax as ceryl palmitate. Palmitic acid crystallizes in tufts, consisting of finely crystallized needles. It is odorless and tasteless, and melts at 62.6°C. It boils with slight decomposition between 339 and 356°C, but distills unchanged under 100 mm. pressure at 271.5°C, and in vacuo at 138-139°C. Palmitic acid is very slightly soluble in cold alcohol, but dissolves readily in boiling alcohol. It is soluble in concentrated sulfuric acid, which/on solution dilution with water precipitates the acid unchanged. Alkaline permanganate oxidizes it to a mixture of acetic, butyric, caproic, oxalic, succinic, and adipic acids. Acids having the composition $C_5H\ O_3$ and $C_{16}H_{32}O_4$ are also formed in this oxidation.

Stearic acid,[1] $CH_3(CH_2)_{16}COOH$, is found in many vegetable and animal fats, notably in cocoa butter and tallow. It occurs also in wool wax. In general, the higher the melting

point of a fat, the higher its stearic content. The acid forms white laminae melting at 69.3°C. It boils at about 360°C with slight decomposition, distilling, however, at 291°C under 100 mm. pressure, at 232°C under 15 mm., and in vacuc at 154.5-155.5°C. Stearic acid is insoluble in water, but diesolves easily in hot alcohol and in ether. Commercial stearic acid obtained by the hydrolysis of fats on a larger scale, consists practically of a mixture of stearic and palmitic acids, and is used in the manufacture of stearine candles.

The chemical change[24] which fats undergo on being saponified is expressed by the following equation:

$$\begin{array}{l} CH_2OR \\ | \\ CHOR + 3\ MOH \\ | \\ CH_2OR \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH + 3\ ROM \\ | \\ CH_2OH \end{array}$$

Where R denotes the radicle of the fatty acid and M the metal whose hydroxide is used in the saponification, usually sodium or potassium. The product R-OM is called a soap, and on adding a mineral acid to the solution, the soap is decomposed, giving the free fatty acids whose radicals are denoted in the equation by R. At a high temperature, water alone can effect the hydrolysis of fats. This reaction is carried out on a large scale by heating fats with water under a pressure of 15 atmospheres (which is equivalent to a temperature of 220°C), or by distilling fats in a current of superheated steam, when fatty acids together with glycerol formed,are carried over by

the steam. Hydrolysis can be accelerated and the temperature reduced, if a suitable catalyst such as hydrochloric acid is present. By treating fats with milk of lime in an autoclave under pressure, only a small amount of the base need be used, as it acts merely as an accelerator. The greater the pressure, the less the amount of lime required. Autoclaves are operated in the modern practice of candle works, at a pressure of about eight atmospheres, three per cent. of lime being employed and giving a practically completely hydrolysed product. The process requires eight to ten hours. In the sulfuric acid, saponification, the dry fat previously heated to 120° or more , is rapidly intermixed with from four to six per cent. of concentrated sulfuric acid of 66-60° Baume. The sulphonated mass is then hydrolysed by boiling water, giving a fatty material of a dark color which is distilled with superheated steam. This process is used almost generally for the treatment of low class material such as "greases" and "waste fats".

The mixed process[24] has been adopted for the treatment of fat of good quality. More candle material is obtained in the "acid saponification" process, while the autoclave process gives a larger amount of glycerol of a better quality, and the two are combined in what is known as the mixed process. The latter consists in autoclaving the fats with bases, thus recovering the full amount of glycerol, and then subjecting the fatty acid material to the sulfuric acid saponification

process described above. This last treatment completely saponifies any neutral fat which has escaped hydrolysis in the autoclave.

Saponification can be effected by means of Twitchell's reagent[24] obtained by allowing an excess of sulfuric acid to act on a solution of oleic acid in aromatic hydrocarbons. If benzene is used, Twitchell describes the product as having the composition $C_6H_4(SO_3H)\cdot(C_{18}H_{35}O_2)$. The composition of the saponifier is kept secret, but the hydrocarbon in the reagent as sold on the market, is known to be haphthalene. The reagent effects an emulsification of the fat, thus greatly facilitating the hydrolysis.

Purified fat is placed in wooden vessels fitted with perforated brass steam coils, and provided with well-fitting lids to prevent access of air to the fat. Fifty per cent. by weight of distilled water is added, along with one to two per cent. of the reagent, and the mass agitated by steam. passing through the brass coil. The Twitchell process utilizes most advantageously, raw fat of low quality and rich in fatty acids, such as "greases" which cannot be economically autoclaved.

The potassium soaps of the higher fatty acids are called soft soaps, the sodium soaps, hard soaps. The processes for hard soap manufacture (described by Pliney) consisted in boiling oils of fats with caustidized wood ashes, the potassium carbonate therein being converted into caustic potash by

boiling with lime.[25] The soap paste thus obtained was repeatedly treated with common salt to convert it into the soda soaps. The following two processes for the manufacture of hard soaps from oils and fats may be outlined as (a) soap making by the cold process, and (b) soap making by the hot process.[24] In the cold process, the fat, previously brought to a temperature of about 35°C, is placed in a large wooden or iron vessel, and an accurately measured quantity of caustic soda of specific gravity 1.35 is run in. The vessel is then covered and allowed to stand, the process of saponification being complete in about twenty-four hours. The quantities of soap manufactured by this process are rather small, most of the commercial soap being made by the hot process.

In the hot process[24] the oils and fats are churned up with dilute caustic soda by means of steam, in large, cylindrical copper or iron pans. On the addition of common salt (salting out) to the soap solution, the water, glycerol, and excess of caustic soda sinks to the bottom of the vessel, and a curdy mass of soap granules rises to the top. From the lower layer, glycerol is obtained. The soap is boiled up with caustic soda solution to insure more complete saponification, again salted out, and finally "fitted", i.e., brought into the condition of finished soap.

The preparation of pure fatty acids presents a rather difficult problem because of the many fatty acids which occur as glycerides in most fats. The problem may be attacked in

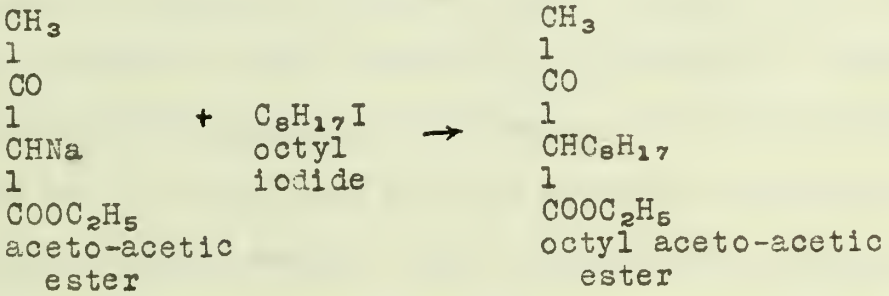
several ways. In the case of the preparation of pure myristic acid, nutmeg butter, extracted with ether from ground nutmegs, or obtained by the hot pressing of the nutmegs, and consisting of almost pure trimyristin, is twice crystallized from alcohol. The product obtained is the pure glyceride of myristic acid, and gives on saponification, pure white myristic acid, melting at 52°C.

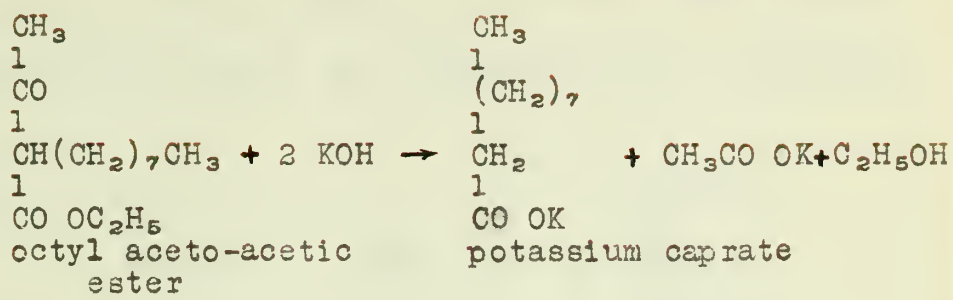
The best source of palmitic acid is bayberry wax, which consists almost entirely of tri-palmatin. The acids obtained from the saponification of bayberry wax, are washed well with hot water, and dissolved in hot alcohol. The alcohol solution is cooled to about 10°C, when a large quantity of palmitic acid crystals separates. The crystals are filtered off with suction , and dried. They give a melting point of 59°C - 60°C. On recrystallization from alcohol, they should melt at 62.6°C, the melting point given in the literature by several investigators. As concentration and cooling of the alcoholic mother liquors gives crystals of impure acids, these liquors may be diluted with sufficient water to precipitate all of the acids as an oily layer . This oil may then be distilled under diminished pressure and further pure palmitic acid obtained.

Methyl esters of the acids of cocoanut oil prepared by Haller's methanolysis method.[26] 500 grams of cocoanut oil is refluxed with 850 grams of dry ether and 650 grams of absolute methyl alcohol containing approximately 2.5% of dry HCl.

After cooling, the HCl is removed by shaking with an excess of barium carbonate, and then washed with strong NaCl solution to remove the alcohol and glycerine. The remaining ether solution is then dried, and the ether distilled off. The resulting esters are fractionated under diminshed pressure, to obtain the pure esters of the fatty acids of the cocoanut oil. The pure esters are then saponified to obtain the acids.

Capric acid was synthesized in 1880 by Guthzeit[27]. He prepared octyl iodide by the action of gaseous hydriodic acid on octyl alcohol, and treated the resulting iodide with the sodium salt of aceto-acetic ester, obtaining thus, octyl aceto-acetic ester. The latter was refluxed for six hours on the steam bath with an excess of strong aqueous potassium hydroxide. The resulting solution shaken up with ether, to remove any oily products formed, the ether layer separated and the soap acidified with sulphuric acid. The capric acid which separated out as an oily layer, was distilled in a vacuum, giving white crystals, melting at 29.5-30°C. The reactions involved, may be expressed thus:

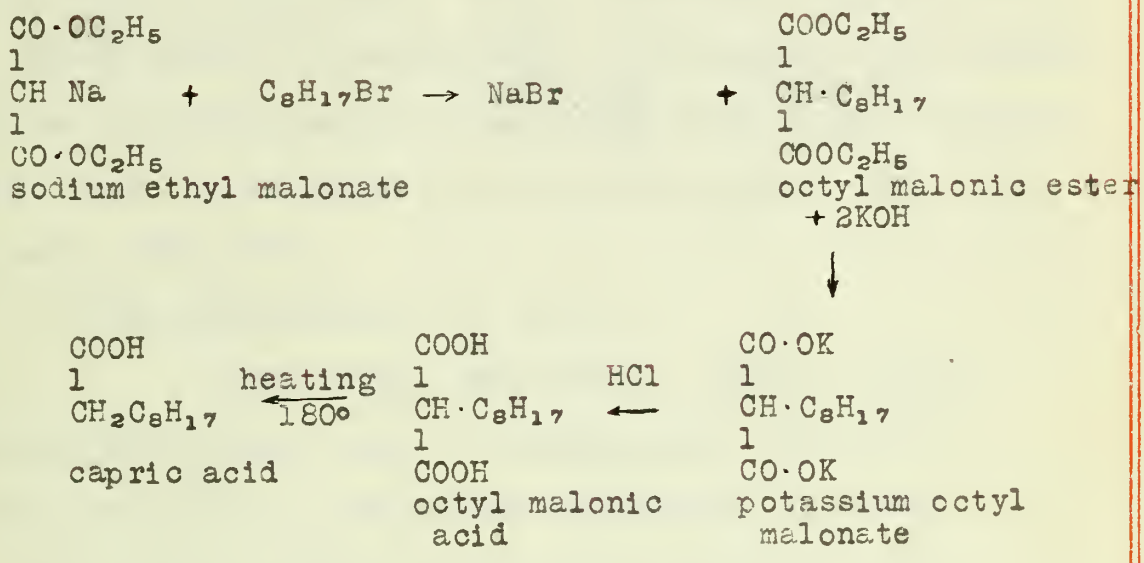




Gerhardt obtained capric acid by oxidizing oil of rue,[28] which contains capric aldehyde, with concentrated nitric acid. Rowney[29] distilled fusel oil, obtaining a mixture of ethyl and amyl alcohols, a dark colored,oily residue remaining. The oil was heated with potassium hydroxide solution,and the soap thus obtained decomposed with sulphuric acid. A dark, oily mass separated. This was dissolved in ammonium hydroxide solution,and the barium soap precipitated with barium chloride. The resulting soap was transformed to the sodium soap with sodium hydroxide, and the latter decomposed with sulphuric acid, giving white solid capric acid.

Beal and Brown[30] synthesized capric acid by the action of malonic ester on octyl bromide. Octyl alcohol was prepared,by reducing ethyl caprylate (obtained from cocoanut oil) with sodium and alcohol. Octyl bromide was obtained by treating the octyl alcohol with phosphorus tribromide. The octyl bromide was heated on the water bath with an alcoholic solution of the sodium salt of malonic ester, thus forming octyl malonic ester. The latter was saponified with potassium hydroxide, the soap decomposed with hydrochloric acid, to give octyl malonic acid.

This acid splits off carbon dioxide at 170-180° C giving capric acid. The steps in the process are expressed by the following equations:



Another capric acid synthesis which was suggested, but not tried out consists in treating lauric acid with phosphorus and bromine, obtaining thus, α-brom lauric acid. The brom-acid gives on treatment with aqueous alkali, α-hydroxy-lauric acid, which on distillation should decompose[31], splitting out formic acid and giving undecylic aldehyde $CH_3(CH_2)_9CHO$. This may be oxidized to give undecylic acid. The processes of bromination, hydrolysis, and distillation, if repeated on the latter, would give capryl aldehyde, which on oxidation would yield capric acid.

THEORETICAL

The first compound to be prepared in the capric acid synthesis is α-brom lauric acid. When a saturated aliphatic acid of the acetic series is treated with red phosphorus and bromine, (Hel-Volhard-Zelinsky method), the α-brom acid bromide results. This acid gives on hydrolysis, the corresponding α-brom acid. Lauric acid reacts thus:

$$3\ CH_3(CH_2)_{10}COOH + P + 11\ Br \longrightarrow$$

$$3\ CH_3\cdot(CH_2)_9\cdot CHBr\cdot COOBr + H_3PO_3 + 5\ HBr.$$

$$CH_3(CH_2)_9\cdot CHBr\cdot COOBr + H_2O \longrightarrow CH_3(CH_2)_9\cdot CHBr\cdot COOH + HBr.$$

The α-brom acids react with sodium ethylate or alcoholic potash, splitting out HBr to give α,β, unsaturated acids. Or they may form hydroxy or ethoxy acids instead of unsaturated compounds. In the case of α-brom lauric acid:

$$CH_3(CH_2)_9\cdot CHBr\cdot COOH + C_2H_5ONa \longrightarrow CH_3(CH_2)_8CH{=}CH\cdot COOH + NaBr + C_2H_5OH.$$

$$CH_3(CH_2)_9\cdot CHBr\cdot COOH + KOH \longrightarrow CH_3(CH_2)_8CH{=}CH\cdot COOH + KBr + H_2O$$

or,

$$CH_3(CH_2)_9\ CH\cdot BR\cdot COOH + C_2H_5ONa \longrightarrow CH_3(CH_2)_9\cdot CH\cdot OC_2H_5\cdot COOH + NaBr$$

$$CH_3(CH_2)_9\ CHBr\cdot COOH + KOH \longrightarrow CH_3(CH_2)_9\cdot CHOH\cdot COOH + KBr.$$

On treating an unsaturated acid with alkaline permanganate, the latter undergoes oxidation at the double union, α,β, unsaturated lauric acid would be oxidized as follows:

$$CH_3(CH_2)_8\cdot CH{=}CH\cdot COOH + 5O \longrightarrow CH_3(CH_2)_8COOH + 2CO_2 + H_2O$$

Or a less complete oxidation and hydrolysis may take place

with the formation of a di-hydroxy acid:

$$2\ CH_3(CH_2)_8CH{=}CH\cdot COOH + O_2 + H_2O \rightarrow 2\ CH_3(CH_2)_8\cdot CHOH\cdot CHOH\cdot COOH,$$

which on further oxidation is usually converted into the lower acid desired.

EXPERIMENTAL

The first problem was the preparation of pure lauric acid as a starting point. For this, a sample of the methyl esters of cocoanut oil (obtained by Haller's methanalysis method) was fractionated at ordinary pressure, and the fraction distilling from 259-264°C was taken to make the acid. 232 grams of this fraction were dissolved in 300 cc. of alcohol, and 90 grams of KOH, dissolved in 50 cc. of water were added slowly with stirring. The alcohol greatly facilitates the saponification, and was subsequently evaporated off on the steam bath. The soap was decomposed with hydrochloric acid in a 5-liter round bottomed flask, lauric acid appearing as pure white flocculated shining plates. It was melted on the steam bath, allowed to solidify, and the mother liquor decanted from the acid cake. The product was melted up and washed twice with water. It gave a melting point 35-40°C.(literature gives 43.6°C). This impure material was used in the following preliminary studies.

The next step in the process was the preparation of the α-brom-lauric acid. This was done according to the method described by Anwers and Bernhardi.[32] 25 grams of lauric acid were intimately mixed with 2.5 grams of red phosphorus, and placed in a one-liter Florence flask. A cork carrying a dropping funnel containing 70 grams of bromine, and a long glass tube to lead off hydrobromic acid formed in the reaction, was inserted in the flask. The bromine was added dropwise, the

time of addition being about two hours. As soon as ten or twenty grams of bromine had been added, the contents of the flask became liquid, and the reaction mixture began to boil quietly. White fumes of hydrobromic acid proceeded up the glass tube. As soon as all the bromine had been added, the flask was gently heated on the steam bath for an hour. Then the excess bromine was driven off by vigorous boiling on the steam bath. The brom-acid bromide thus obtained, is a syrupy, yellow liquid, fuming when exposed to the air. It was slowly added from a dropping funnel to a large volume of water, with constant agitation. The brom-acid bromide is hydrolysed by this treatment to α-brom-lauric acid which separates, and sinks to the bottom of the flask as a yellow, viscous oil. On cooling, the acid solidified, forming wart-like crystals of a yellow color. The water was decanted, and the crystalline cake broken up and placed in a vacuum dessicator over calcium chloride. It melted, however, below room temperature and therefore could not be plated out. Anwers and Bernhardi give the melting point of α-brom lauric acid as 30-31.5° C.

A ten gram portion of the brom-acid was refluxed with sodium alcoholate (made by dissolving 1.2 grams of sodium in absolute alcohol) on the steam bath for 48 hours. The resulting mixture was diluted with 150 cc. of water, and the alcohol boiled off on the steam bath. The soap was acidified with hydrochloric acid, giving a fine, white precipitate which melted at room temperature and floated on the top as a golden, yellow oil.

Another ten-gram portion of brom-lauric acid was similarly treated, using a large excess of sodium ethylate (4 grams of sodium in 100 cc. of absolute alcohol), the time of refluxing being, in this case, only 26 hours. The acid obtained in this trial was a clear, lemon-yellow oil which could not be solidified on cooling with an ice and salt mixture. The acid obtained in the other run, solidified on cooling, giving a mushy, yellow solid, probably containing some unchanged brom-acid. Neither of the samples of acid could be crystallized from alcohol, even on thorough cooling with a freezing mixture. Neither of the samples, dissolved in ether, gave a test for unsaturation with an ether solution of bromine.

A small test portion of the unsaturated acid was dissolved in 10% sodium hydroxide solution, and a little saturated potassium permanganate solution added. A brilliant green (manganate) color appeared, and on heating the solution, further reduction of the permanganate took place, with the formation of brown hydrated manganese dioxide. The solution was boiled vigorously, permanganate solution being added from time to time as the green color disappeared. After six hours heating on the steam bath, no further action could be seen to take place, and the brown, hydrated oxide was filtered off. On acidifying the soap solution, with HCl, a colorless oil appeared on top of the solution. It was extracted with ether, the ether extract dried with anhydrous sodium sulphate, and the ether evaporated. The resulting compound was a colorless oil, which solidified

on cooling with a freezing mixture to a creamy-white mass. No characteristic crystals of capric acid were noted, however. The acid melted somewhere below room temperature and gave a mean molecular weight of 189.2 (capric 172).

It was concluded that the fact that the lauric acid used as the starting point was impure, occasioned difficulties and gave impure products in the different steps of the synthesis. Therefore the logical step seemed to be the preparation of pure lauric acid. Accordingly, a fractionation of the ethyl esters of cocoanut oil (obtained by the aforementioned Haller's method) was carried out. The fractionating flask used, was a modified one-liter Claissen flask, the neck of which had been carefully heated, and indentations made in the same with a sharp pointed instrument, thus forming a very effective fractionating column. The fractionation was carried out under diminished pressure maintained with an electrically operated oil pump. About 700 cc. of the ethyl esters were introduced into the flask, the pressure reduced to 12 mm., and the flask gently heated. The distillate began to come over at 120°C under 12 mm. pressure. The temperature was gradually raised until 150°C was reached. Then the fraction was cut, and the fractions distilling at from 150-160°C and from 160-170°C collected separately. A pressure of 12 mm. was maintained throughout this first fractionation. The greater part of the liquid distilled between 135-145°C, under 12 mm. pressure. Five separate fractionations were made, separating the distillates into the three ten-degree

fractions described above. As the boiling point of ethyl laurate under diminshed pressure could not be found in the literature, test samples of the first and second fractions were saponified, decomposed with hydrochloric acid, and the melting points of the acids thus obtained, determined. The melting point of the acid from the saponification of the sample of the first fraction was 36-39°C. The acid obtained from the second fraction sample was very impure, and remained liquid at room temperature. It was concluded that the first fraction (120°-150°C under 12 mm. pressure) contained the ethyl laurate. This portion, having a volume of 850 cc., was therefore refractionated, and separated as follows:

Fraction Number	Temperature Range °C	Pressure Millometers
1	120-130	10
2	130-135	10
3	135-140	10
4	140-145	10

The fourth fraction comprised by far the larger part of the distillate. The most constant temperature noted was the range 142-143.5°C under 10 mm. pressure, and this was taken as the boiling point of ethyl laurate. A test sample gave, on saponification, an acid melting from 41-43.5°C, and having a mean molecular weight of 200.5 (theoretical 200). 305 grams of the ester obtained from the fourth fractionation were saponified in three portions, by heating on the steam bath with a slight excess of potassium hydroxide. The saponification can be carried out just as well without the use of alcohol as a solvent for the ester, except that a little more time is required for

the reaction if alcohol is not used. From the saponification, 250 grams of pure, white lauric acid were obtained. The product had a melting point of 40-42.5°C.

100 grams of the acid were brominated, using red phosphorus and an excess of bromine as described above. The brom-acid bromide obtained was hydrolysed by dropping it slowly into hot water. The brom-acid from this reaction was of a golden yellow color, but when plated out, it was pure white and had a melting point of 28-30°C. Clay plating occasions, however, considerable loss of the acid by melting and absorption by the plate, and the main portion of the product was therefore not plated out, but merely dried over calcium chloride in a vacuum dessicator. The acid should be kept out of contact with air, as it becomes brown on standing exposed to the air, due probably, to partial decomposition and liberation of bromine, or to dissolved impurities. The hydrolysis of the brom-acid bromide should be effected by dropping the product into hot water, for if cold water is used, the brom-acid on heating the mixture, rises to the top of the water as a fine, flocculent-emulsion which is very hard to break.

In the unsaturation experiment, 20, grams of α-brom lauric acid were refluxed for two hours with dry sodium ethylate. (Kahlbaum's alkohol frei), 100 cc. of absolute alcohol were then added, and the mixture heated for another hour, when 75 cc. of freshly prepared, syrupy sodium ethylate were added. The

mixture was refluxed on the steam bath for twenty-four hours. At the end of that time the alcohol was distilled off, leaving a clear,yellow residue, which was dissolved in water to give a pale, honey-colored solution. To this solution was gradually added a calculated amount of potassium permanganate solution, (3 mols. acid: 8 mols. permanganate) with heating on the steam bath . The hydrated manganese dioxide formed, was filtered off with suction, and the solution acidified with hydrochloric acid. The resultant acid separated as a milky suspension and was removed from the solution by extraction with ether. The ether extract was dried over anhydrous sodium sulphate, and the ether distilled, leaving a colorless oil, which could not be solidified by cooling with a freezing mixture of ice and salt. The latter was distilled under diminished pressure, the major portion of the distillate coming over between 130° and 146°C under 5 mm. pressure. This product solidified on cooling in beautiful, needle crystals, characteristic of capric acid, and possessing the peculiar goat-like smell of the latter. It melted slowly, however, at room temperature and gave a mean molecular weight of 186 (theoretical 172). The yield was about 3 grams.

In order to study properties of unsaturation of the acid prepared by treating α-brom-lauric acid with alcoholic potash, a portion of that acid prepared as above, using alcoholic potash in place of sodium ethylate, was distilled under diminished pressure. Large volumes of white fumes came over until

a temperature of 138°C under 14 mm. pressure was reached. At this point, a colorless oil distilled over. Different fractions were collected, and at 183° under 12 mm. pressure, the liquid was solidified in the condenser, and the vapors condensed as white, flocculent flakes. The different fractions and their refractive indices at room temperature are listed in the following table:

Fraction No.	Form	Refractive Index
1	colorless oil	1.4430
2	colorless oil	1.4420
3	yellow oil	1.4455
4	yellow solid	1.4462

The refractive index of lauric acid is 1.42665 at 60°C, and that of capric, 1.42855 at 40°C. The higher refractive index of the above fractions of the acid obtained, indicate a certain degree of unsaturation. The iodine number of the third fraction was 11.49. Lewkowitsch[33] states that in the case of some unsaturated acids, the theoretical amounts of iodine is not absorbed, but he confirmed the fact that all glycerides and fatty acids which occur in the commercial analysis of oils, fats, and waxes, do conform with the theory. In order to determine whether or not hydroxy acids were present in the unsaturated acid, a small portion (0.2 gram) in 10% NaOH was submitted to the action of para nitrobenzoyl chloride (Schotten-Baumann

reaction). On acidifying the solution a white precipitate resulted, the latter being recrystallized from 50% alcohol. The crystals proved to be p-nitro benzoic acid, and an ether extract of the acidified aqueous solution, gave no benzoyl compound on evaporating the ether. It was therefore concluded that no hydroxy acid was present in the sample.

CONCLUSIONS

Lauric Acid can be easily prepared by the saponification of ethyl or methyl laurate obtained by Haller's ethanolysis or methanolysis method from cocoanut oil. The boiling point of ethyl laurate is 142-143.5°C under 10 mm. pressure.

α-brom lauric acid is obtained by brominating lauric acid with phosphorus and bromine, and hydrolysing the resulting brom-acid bromide. In the latter process, hot water should be used to avoid the formation of troublesome emulsions of the brom acid formed. The latter should be kept in a vacuum dessicator over calcium chloride, as it decomposes slightly when exposed to air.

α,β, unsaturated lauric acid results, in part, when αbrom lauric acid is refluxed with sodium ethylate or alcoholic potash. A larger proportion of the unsaturated acid would probably be formed if the reaction were carried out in a sealed tube. As prepared, the acid no doubt contained certain quantities of ethoxy, mono and di-hydroxy lauric acids, formed by side reactions.

Capric acid is formed along with some of the lower members of the acetic series, when α,β, unsaturated lauric acid is oxidized with alkaline potassium permanganate.

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